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A TECHNICAL MAGAZINE

Vol. XXIX MARCH, 1949 No. 3

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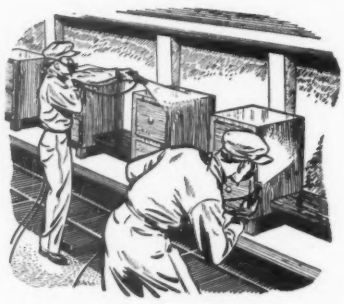

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A TECHNICAL, EDUCATIONAL AND PRACTICAL JOURNAL FOR THE PRODUCTION MANAGER

Founded September, 1928

Comprising
"The Paint and Varnish Record"
Founded in 1911

Entered as Second-class matter, May, 1935, at the Post Office at Washington, D. C. Under the Act of March 3, 1879.

Published the First of Every Month by Paint and Varnish PRODUCTION MANAGER

Member, Oil and Colour Chemists' Association, London, England.

M. R. DRAKE, *Publisher*
EDWARD R. DRAKE, *Editor*
Publication Office
Mills Building, Washington 6, D. C.

DUNCAN P. MACPHERSON
Advertising Manager
700 So. Washington Square
Philadelphia, Pa.

See Standard Rate and Data Service for rates. Advertising copy expected the 10th of each month.

Subscription price per year in the United States, $3.00; Canada and other Foreign Countries, $3.60; payable in advance.

MECHANISM OF PIGMENTATION OF ANTI-CORROSION PAINTS AND VARNISHES

By DR. HANS WAGNER

CONTENTS: The electrochemical evaluation of anti-rusting pigments—Protection through over-activation of iron surfaces—Protection by passivation and oxide-skin formation—Cathodic and anodic effects of pigments—Evaluation of anti-rusting pigments—Comparison of recent results of Wirth, Scheifele, Grube and Wagner.

If the various series of evaluation of anti-rusting pigments published in technical literature by authorities such as Cushman, Evans, Lewis, Nelson, Blom, etc., are carefully compared it will be found that they agree but very little with each other. The only favorable exception are red lead and the pigments containing lead oxide, while the most pronounced discrepancies are found with pigments such as lead chromate, graphite, aluminum and the oxides of iron. Another discouraging factor relative to these published values is that they show very little agreement with the protective effects observed in actual exposure tests, and this factor alone appears to confirm the supposition that electrochemical anti-rusting protection does not influence the final results nearly as much as is frequently supposed.

The problem therefore arises as to the extent to which electrochemical viewpoints may enter into a general evaluation of the anti-rusting protection afforded by the various pigments or pigment mixtures under actual conditions of exposure. Studying this problem of electrochemical pigment action more closely we have to consider the following four possibilities:

1) *Induction of a super-active state by the cathodic polarisation of iron*: This is possible only in presence of strong alkalies exhibiting a pH-value > 8. A comparatively high degree of alkalinity of this type is exhibited only by oxide of lead, red lead and dibasic chromate of lead. If, therefore, red lead actually exerts an electrochemical effect or if such an effect becomes active in red lead paints, super-activation of iron surfaces may really be possible. It has been attempted to saturate highly surface-active pigments such as carbon black and active carbon with ammonia in order to obtain similar effects. Attention must be called to the fact, however, that pigments of this type are characterized by a strong positive swelling factor, inducing a comparatively slow rate of drying and a reduction of the strength characteristics of the films produced. This does not mean that these pigments are bound to be inactive and that the less favorable paint-technical properties outweigh the improved electrochemical effects, but there is the danger of overstressing the paint films in question if they have to bear the full stress of mechanical protection. Practical experiments have indicated beyond doubt that such pigments must be protected with top coats proof against swelling, sulphurous acid vapors and weather conditions and that this protective influence is most pronounced if the top coats contain suitable lead pigments. It is thus obvious that the savings effected in compounding the priming coats must be sacrificed in making up the top coats.

2) *Passivation by means of oxide-skin formation*: The large importance of the passivation of iron surfaces and the formation of an oxide skin

exhibiting a minimum degree of porosity by means of crystallizing effects at the metal surface has been stressed in a number of recent reports on electrochemical research work conducted by W. J. Mueller and J. K. Wirth. A passivating influence of this type is usually ascribed to red lead.

Previously it was held that this effect of red lead is due to the superoxide contents and that the effectiveness of red lead in this respect must be judged on basis of the superoxide contents. However, this assumption has been disproved completely. Indeed, Ragg proved that iron is strongly corroded by Pb O_2 and that therefore this compound cannot be the real reason for the rust-protecting effect of red lead.

Different conditions prevail in the case of the chromates, literary information on this subject being particularly erratic. It is well known, of course, that soluble chromates tend to produce oxide skins. It is very dangerous, however, to introduce the chromates into the paint films even if, according to Blom they are adsorbed by carbon black, silica gel, etc. (German Patent No. 667,135) since they tend to behave like the ammoniacal active carbon mentioned above. The chromates introduce another difficulty, however. Experiments have shown that in spite of suitable adsorption reactions soluble chromates tend to penetrate (bleed) even through the top films.

Insoluble or even difficulty soluble chromates behave differently. They cannot exert a direct passivating influence irrespective of whether they react neutral or basic. It is not impossible, however, that in presence of moisture or water of any kind hydrolysis may exert a reducing effect, causing the liberation of oxygen which may oxidize the lead oxide formed to lead peroxide such as is indicated by the well known blackening of the films under the influence of light. These reactions may also explain a passivating influence, however, although the latter can develop only after a rather pronounced destruction of the film structure, deteriorating the adherence and strength of the paint films accordingly. There can be no doubt, therefore, that chromates of this type do not offer any considerable advantages in this direction.

Much better results have been obtained with zinc chromates in practical as well as electrochemical respects, although the method of production of these chromates play a very important part in determining the characteristic effects in question. The modes of production of the zinc chromates give rise to products of considerable difference not only regarding the degrees of solubility but their compositions as well which may fluctuate between those or the simple double salts and of the complex salts of varying compositions, frequently including a considerable percentage of zinc oxide. It is possible that particularly the zinc oxide contents of these compounds may be important in causing the favorable rust-protecting effects of these products.

It has also been shown that a zinc chromate with considerable zinc oxide contents is superior to the ordinary zinc chromate (German Patent No. 644,036—H. Wagner). Zinc chromate also differs from lead chromate in its easier reducibility, especially in presence of organic substances. The pronounced "greening" of the oil films containing zinc chromate proves the high degree of reducibility of these compounds. Since potassium is also contained in their molecules, lyes can be formed, so that apart from a passivating influence at some points not covered with oxide film superactivation may also take place.

Attention should be called to the fact, however, that Ragg determined a pronounced deteriorating influence of electrolytes on chromate. In comparing the effects of zinc chromates in alkyde resins on one side and in linseed oil-boiled oil on the other, it becomes obvious that the former are the most favorable. This points to the fact that a low degree of swelling capacity and comparatively high weather resistance favor the influence of zinc chromate, i.e., conditions acting against the reduction of chromate.

3) *Differences of Potential*: a) Pigments less noble than iron. It is well know that iron is protected by direct contact, or through the action of electrolytes, with metals less noble than iron. This applies to zinc, aluminum and magnesium. It is also well know, however, that zinc dust has not come up to expectations in this respect. This may be due to the fact that the potential difference Fe/Zn does not suffice in face of the resistance of the surface skin. It is also possible, however, that the surface of these pigment powders is not sufficiently metallic, while the most probable conclusion is that no local currents are developed within the films at all. If electrochemical reactions actually take place, conditions would be more favorable for aluminum and magnesium, and this is actually confirmed in the case of aluminum and aluminum-silicon alloys. It is obvious, of course, that mixtures of aluminum and lead pigments are nonsensical for a number of reasons.

b) Pigments nobler than iron. While in the case of the pigments less noble than iron passivation is impossible since only anodic iron can really be passivated, passivation is possible in principle

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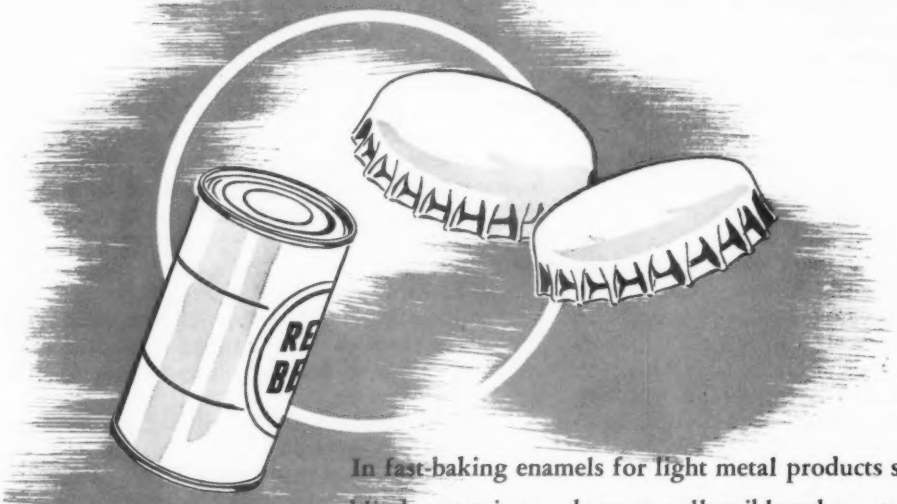

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wherever iron becomes a soluble anode within the electrochemical system. And this applies to all systems of iron with metals nobler than itself.

However, the action of the local current alone increases the danger of rust formation, although as a whole it is not very pronounced even in this case. Besides lead, most of our pigments including red lead, oxide of iron, white lead and even zinc oxide react electro-positive toward iron without indicating any deteriorating influence in this respect. This too has been explained by Ragg with the insufficiently high potential difference in face of the resistance of the surface skin. It can be stated in any case that metals nobler than iron will hardly exert deteriorating influences in this respect. Indeed, according to Wirth (Korrosion und Metallschutz, 16 (1940) p. 331) the pronouncedly favorable effects of some oxides of iron are due to anodic oxidation, although he does not explain why rust is produced instead of oxide skins in presence of other iron oxides.

Mention should here be made of the possibility of "lead plating" suggested by some authorities in connection with the use of lead compounds in paints. It is true that in principle lead superoxide is reducible by ignobler metals, and one may therefore be justified in raising the question whether this reduction could not possibly be continued down to metallic lead. It should be considered, however, that lead plating is not effected on an oxide skin and that on a hydrogen-iron alloy the hydrogen would first have to be oxidized to water. Very little has been heard of "lead plating" reactions of late, and there can be no doubt that the high degree of efficiency of the anti-rusting pigments of Blom and Ragg can be satisfactorily explained without taking recourse to this possibility.

A much more important problem which has never been satisfactorily solved as yet is whether electrochemical reactions are possible in normal paint films at all. It is useless in this respect to point to the doubtlessly existing ionic penetrability of the films since this does not prove any possibilities of contact between pigment particles and the iron surface. A "normal" paint film must be considered a combination film in which the priming coat is covered with a satisfactory top coat and in which both coats the constructed so that satisfactory chemical and mechanical properties are obtained. Although the ionic penetrability through the protective films renders some kind of a connection between oxide skin and hydrogen-iron alloy probable, this does not apply in a similar degree to the contact between pigments and iron surface.

The experiments conducted by Wirth have shown that the penetrability depends on the direction of the electrochemical current, thus being different for different ions. However, the measurements require the presence of a counter electrode. If this is not the case or if the difference of potential between pigment and iron is not sufficiently large, the existence of local currents is improbable. Another requirement is the presence of water and of electrolyte. It is true that water might be present even within the pigments and may be split off from hydrates and hydrogels. Water may also be absorbed in the vehicle or be liberated by decomposition or other reactions, which may also cause the production of oxygen, free acids and peroxides.

However, the development of electrochemical effects of this type require a rather high degree of penetration through the entire thickness of the film such as is absolutely improbable in fresh films suitably protected by top coats. It is true that during normal ageing of the films conditions gradually become more unfavorable but if vehicles and the composition of the top coat material are entirely satisfactory conditions will remain favorable for a long time. There can be no doubt that pronounced electrochemical reactions between film contents and iron surfaces can take place only after the structure of the film has been so considerably deteriorated that these reactions, or the possible unfavorable effects induced by them, are practically insignificant in comparison with the other difficulties such as especially the decline of adhesion of the films.

In a paper recently published by Scheifele ("Farben-Zeitung", 45 (1940) p. 840) he expresses the opinion that anti-rusting paints must exhibit a high pigment-vehicle relation in order to cause direct contact of a large proportion of the pigment particles with the metallic surface without excessive interruptions of such points of contact by thick oil films. However, this pigment-vehicle relation is a function of the degree of brushability of the paints applied. The vehicle contents should not drop beyond a point approximately corresponding to the flowing point of the paint, adding sufficient volatile thinner—if necessary—to obtain satisfactory spreading free from brush markings.

If electrochemical reactions really would play an important part, it would doubtlessly be more favorable to add non-fluid vehicles in only sufficient quantities to attain the smearing point, followed by addition of suitable solvents until the required state of brushability is attained. Similar results can also be obtained with the use of water-oil emulsions. If the degree of adherence of these products is sufficiently high they ought to exert a greater anti-rusting effect on iron surfaces than most of the normal combinations, provided that the top coat is compounded and applied so that it is able to protect the priming coat against all mechanical stresses. I do not know whether experiments along these lines have already been carried out.

If crossections of antirusting films are studied under the microscope, the pigments usually appear in form of dense, grained agglomerates enclosing large hollow spaces and pores. It is quite probable however that the agglomerates them-

selves are so dense and so perfectly wetted that they do not permit direct contact of the pigment particles with the metallic surfaces.

Attention should in this connection be called to the pronounced difference between inter-micellar and intra-micellar swelling. The swelling resistance measurements devised by Scheiber refer to intermicellar swelling, while the other type of swelling, intramicellar swelling, pertains to the pigment-iron contact relations in question. This fact is of great practical importance and calls for considerable caution in the evaluation of inoic penetration measurements. It also indicates that the non-electrochemical properties of anti-rusting paint films are of greater importance, a fact clearly confirmed by the action of red lead. It has been shown that in the case of red lead electrochemical effects are clearly overshadowed by purely chemical and mechanical-physical processes. It is true that for a certain restricted period red lead tends to increase the potential, but it has been shown by the work of Grube that the iron potential gradually becomes stable again, so that the electrochemical effects—if exerted at all—cannot be of long duration.

Our observations thus lead us to the much discussed problems concerning the reactions between pigments containing lead oxide and the various components of the fatty oils. There can be no doubt whatever that the final outcome of these reactions represents a very important improvement of adherence and swelling resistance of the films produced as well as, probably, of the degree of elongation and resilience and of the chemical resistance of the coatings, no matter whether these reactions consist of actual saponification accompanied by the separation of glycerine or of reactions of free fatty acids separating water or whether they represent preliminary steps to the adsorption of fatty acids.

These reactions and their final effects are so important in any case that the favorable effects of lead pigments suffice in practically all cases if the weather resistance of the top coats is satisfactory.

Laboratory experiments have shown that the formation of visible products of reaction between red lead and fatty acids is supported by increased temperatures and short-wave light rays. Can it be an accident, that red lead exhibits a high degree of heat penetration and that a red lead-oil film is highly transparent if held up against the light? While at the same time the tinted white lead film usually employed as top coat also exhibits a comparatively high degree of light penetration? Freshly applied red lead films exposed to Uviol light shows a considerable increase of hardness without corresponding decreases of elasticity and adherence, and all this in a degree not observed in any other pigment.

It may well be concluded from this observation that a certain amount of penetrability to heat and light is required to obtain satisfactory strength values of anti-rusting paints containing red lead.

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If this conclusion applies it is not at all immaterial whether the red lead mixtures are cut with heavy spar or some covering pigment.

There can be no doubt that cutting additions of this type are not only of economical advantage but that they are also quite important mechanically. This fact has been proven by numerous laboratory and scientific experiments as well as by long years of experience with anti-rusting paints. The author himself conducted experiments of this type for more than five years subjecting all kinds of paint mixtures to all imaginable weather conditions in city-, country- and industrial atmospheres, including the chemically contaminated atmospheres at Leverkusen (Germany). The experiments were conducted with priming coats freely exposed and covered with various types of top coats and it was found that good results are obtained with red lead paints containing 50 percent of heavy spar. The results obtained by the author indicate that 50% of heavy spar should not be exceeded while the results obtained by Scheiber with his so-called swelling resistance measurements seem to point to the fact that red lead yields satisfactory properties with heavy spar contents of up to 80 percent.

There can be no doubt, however, that the degree of penetrability to light rays and the favorable shape of the spar grains alone determine the cutting capacity of the heavy spar. Years ago the author expressed the opinion that the reduction of reactive PbO favors the formation of a mechanically desirable soap structure, and the innumerable results of modern investigations and practical observations seem to confirm this theory. An interesting comparison illustrating the mechanism of this reaction is the strengthening influence of asbestos fibres in cement or concrete. It is quite immaterial whether the products of reaction do, or do not, form quite as beautiful spherolithes as are usually exhibited in books or in lectures by means of polarized light. Isotropical colloid skeletons are also able to develop favorable effects of the same magnitude while in regards to elongation and resilience values they are even superior to the anisotropical formations.

The discussion of the lead soaps was not confined to red lead alone because it represents an important factor in all pigments containing lead oxide. In pigments containing moderate amounts of PbO the general results are just as favorable as in the case of red lead, although the high speed of reaction induces the danger of thickening of the mixtures. It is perfectly possible, however, to produce anti-rusting paints of moderate lead contents with PbO which are quite as active as red lead mixtures and in which the danger of thickening is reduced by suitable additions such as the use of water-in-oil emulsions. It has been proven beyond doubt that the water present in form of water-in-oil emulsions exerts a strong delaying or even eliminating effect on the chemical reactions between the pigments in fatty oils.

It is also known for a long time that on account of their greater degree of brittleness and their lesser resistance toward hydrolysation zinc soaps are not as favorable as lead soaps, but it is also proven that zinc oxides may exert valuable protective effects either through their reactions with fatty acids or through neutralization of the lower acids of decomposition. It is quite possible that the favorable anti-rusting effects of zinc chromates containing considerable quantities of zinc oxide are due to these reactions.

Comparatively little is known about the properties of aluminum soaps, and since aluminum doubtlessly belongs to the useful anti-rusting pigments it appears advisable to study this question more closely.

Referring to the lead chromates it is a very peculiar fact that the age-old erroneous opinions concerning the saponifying properties of basic lead chromate cannot be eliminated from technical literature. The author has been able to show years ago that PbO or $Pb(OH)_2$ are chemically inactive in combination with chromate, a fact due to structural reasons. It is not impossible, however, that due to the action of light and reducing agents the chromates are decomposed in such a way that they may become active later on. Nevertheless, it is quite doubtful whether the soaps thus produced exert any useful activity.

Different conditions prevail if according to the German Patent No. 672 379 (by H. Wagner and H. Schirmer) a dibasic chromate—2 $PbO.PbCrO_4$—is produced which for the same reasons acts as $PbO.PbCrO_4$ + PbO but which differs considerably from common mixtures of this composition by a number of important properties such as, for instance, less pronounced thickening tendencies. A chromate of this type will be found equal to red lead, its pH-value exceeding 9. On account of its chromium contents this compound has no practical importance in Germany to-day (Scarcity of chromium).

There actually exist a few pigments which may really be considered inactive in every chemical direction, but which exhibit a very pronounced anti-rusting effect nevertheless. The most peculiar of these pigments doubtlessly is iron mica characterized by its scaly structure. It cannot be denied that this scale structure, if well orientated within the film, may induce a high degree of adherence and, especially, elongation combined with good resilience. If two scaly pigments, iron mica and aluminum powder are mixed, the increase of anti-rusting action is probably not due to their uniformity of structure but to the fact that the spaces between the individual scales are filled and cemented by aluminum soaps.

The ionic penetration of the films containing iron mica is considerably decreased, of course, as has been scientifically proven, or confirmed, by the curve tables published by Wirth ("Chemische Fabrik", 11 (1938) p. 455). These tables and the results of his experimental work indicate, how-

ever, that after a certain time of exposure the resistance against ionic penetration decreases very considerably. If we consider the aging processes within a film during the first ten days after application it will be found that it is possible without any electrochemical effects and solely due to favorable shape of grain to considerably reduce ionic penetration if the vehicles exhibit only moderate swelling resistance. This proves that factors such as shape and size of pigment grains, oil requirements and the packing of the pigments within the films play an important part in determining the anti-rusting qualities of the paints.

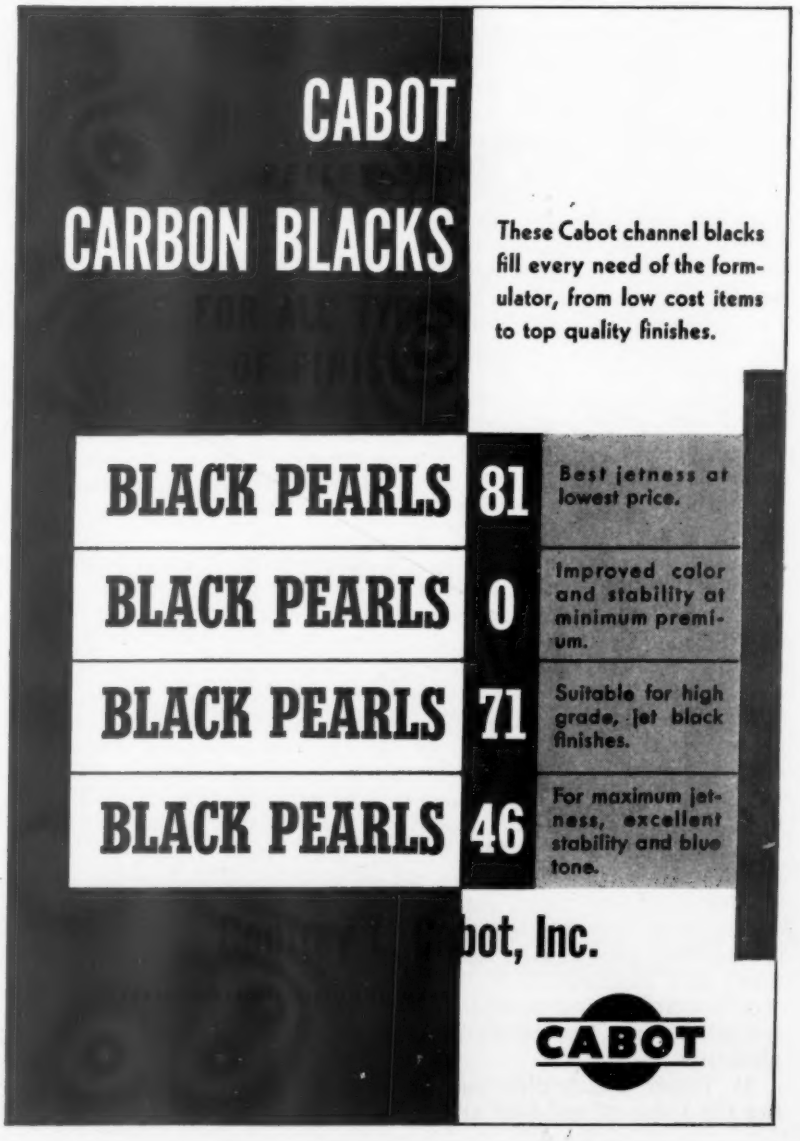
It has been claimed that the anti-rusting effects of magnetite (quartz-free) which is sometimes traded as hammer scale (iron oxide) as well as of real hammer scale is due to ferro-magnetism and to the adherence induced thereby. However, this not the case since ferro-magnetism has little to do with the degree of adherence of the films. The favorable effect of these substances is merely due to the structure of these pigments, the same as in the case of mica. The same applies to silicon carbide as a pigment used in connection with anti-rusting paints.

The improvement of the effects of iron mica additions by suitable mixtures with scaly aluminum powder proves that the purely mechanical protection of certain pigments should be enhanced by a sufficiently large percentage of active substances such as red lead or lead on one hand or of aluminum or zinc on the other.

The influence of the chromates also assumes greater importance in this connection. Experiments conducted with non-saponifiable neutral lead chromates have shown that as additions to iron oxide pigments in linseed oil —boiled oil — as strongly swelling vehicles — these chromates tend to increase rusting of iron surface in spite of the improved chances of passivation by oxidation. If the same chromates in connection with the same iron oxide pigments are used with alkyde resins, however, rusting of iron surfaces is considerably reduced. Least effective in this respect were the finely dispersed, grained, rhombic lead chromates. More pronounced anti-rusting effects are exerted by finely acicular, chiefly monoclinic lead chromate, while best results were obtained with the coarsely acicular, purely monoclinic chromate. (DRP.No.630 660—H. Wagner). Since all these lead chromates are of practically identical chemical composition, it must be the shape of the pigment grains which exerts the protective influence in question.

Recapitulating the various points discussed above we arrive at the following *conclusions*:

1) The importance of the ionic penetration capacity of a film must doubtlessly be realized, but this fact should not be used as proof of pigment/iron contacts or of any electrochemical reactions in general. Since it appears hardly possible to induce complete closing of pores by means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of paint films and since formation of oxide skins through the action of passivating pigments seems quite unlikely as a whole, the processes of surface treatment with passivating solutions such as, for instance, the phosphatizing processes should be still more carefully studied. These processes have now been perfected to such an extent, that they can be applied even to large surfaces without application of heat. However, it is still necessary to study the development of the most suitable pigments and paint combinations used as protective coatings for the oxide films produced on the iron surfaces by these processes.

2) As long as there are still technical difficulties in carrying out these chemical processes under all practical conditions it remains necessary to rely on the anti-rusting protection by paint films. If this problem is studied as a mere pigment problem, there can be no doubt that the lead pigments reacting with fatty oils are the most advantageous. The chances to get away from the lead pigments entirely and to find high-grade specific anti-rusting pigments of other compositions are much less promising than the chances of obtaining suitable pigment mixtures consisting of relatively small quantities of active lead pigments and larger percentages of suitable auxiliary pigments. This means that lead pigments should not be entirely eliminated but that considerable savings in that direction can be effected by suitable cutting with heavy spar. It is desirable to conduct further confirmatory experiments in this direction. It is possible that plated pigments (such as are caused by chemical or electrochemical reduction of lead compounds) may exert a favorable influence on general results, besides effecting a considerable saving of active pigments (a very important feature in European countries today), but the processes published heretofore have not cleared up our serious doubts regarding the practical possibilities of such plating reactions.

3) The electrochemical effects of pigments are not of determining importance with regard to the behavior of anti-rusting paint films but may exert an additional, or auxiliary, influence on the anti-rusting properties, besides delaying the unfavorable effects of the ageing processes taking place within the films. Where electrochemical influences really do exert themselves, the presence of certain quantities of water may be favorable regardless of whether this is already present in the fresh films or whether it is produced by reactions within the coatings. It is necessary in this case, however, to increase the protective capacity of the top coating without overstressing the latter. Nevertheless, it is to be assumed that the structure of the films with regard to the pigment arrangement and the formation of strengthening and stress-compensating products of reaction is more important than the electrochemical effects of the pigments.

4) There is little difference of opinion regarding the value of red lead and some other special pigments containing lead in connection with iron mica and aluminum powder. It is not yet quite certain why certain oxydes of iron are particularly effective in this respect.

There is considerable difference of opinion, however, on the effectiveness of other special pigments containing no lead. It is absolutely necessary for this reason to test them all by the various standard methods and under the numerous conditions involved and to compare results. It would then be possible to come to definite and generally acceptable conclusions concerning the respective values of these pigments as well as to the value of the various short-testing methods applied.

5) Particular attention must be paid to the structure of these films and to the relation of the priming coats to the top coats. It is clear that every type of priming coat requires a suitable top coat and vice versa, and that for this reason it is impossible to speak of certain priming and top coat pigments or pigment combinations suited equally well for all purposes. The distribution of functions of the two coats depends on the specific properties of the individual pigments. The laws on which these relations are based are not entirely determined as yet and should therefore form the subject of further detailed investigations.

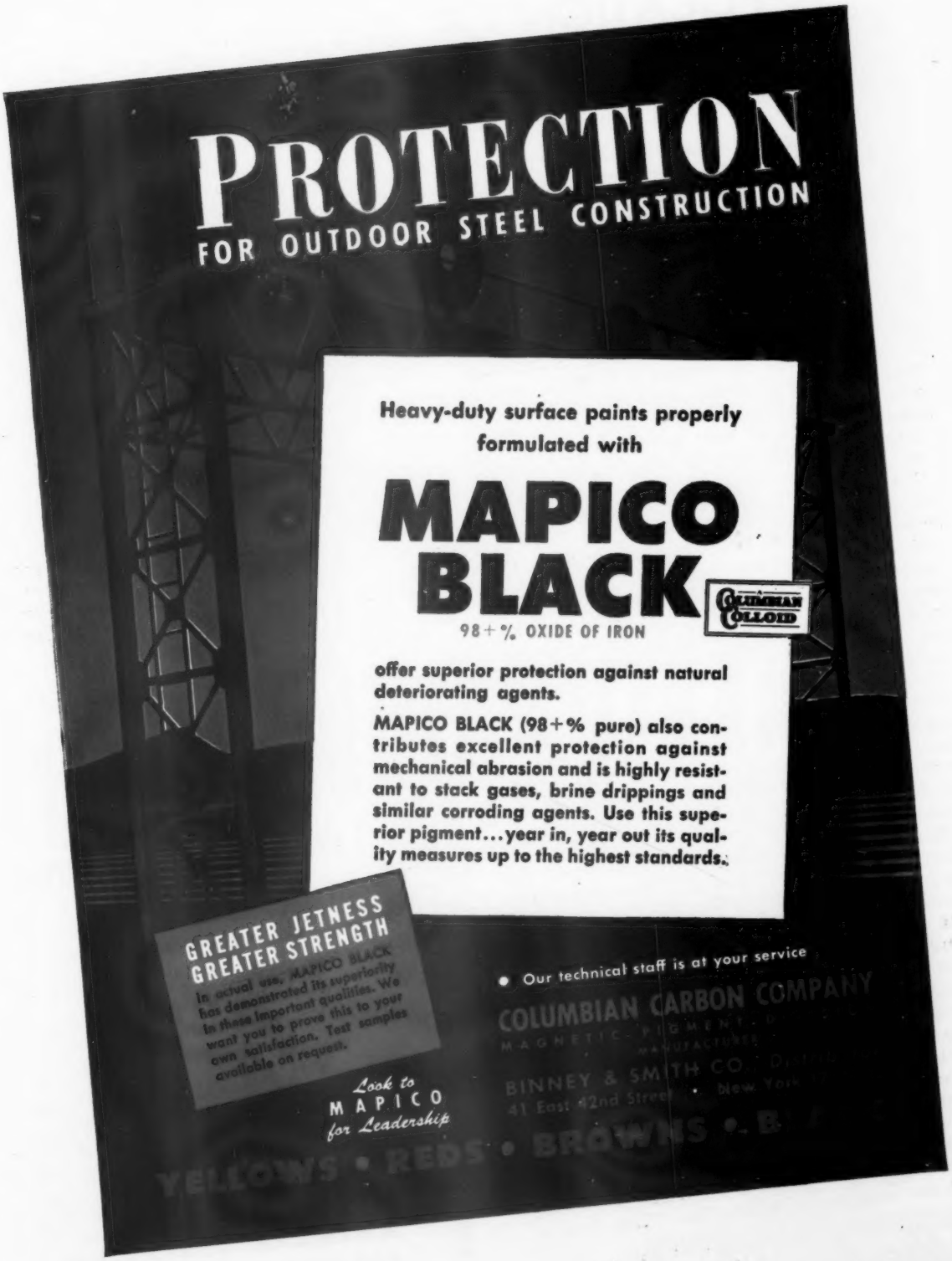
6) The evaluation of anti-rusting pigments can never be based on single electrochemical laboratory tests or on certain individual arbitrarely selected tests such as, for instance, covering power, resistance to acids, hardness of films produced, oil requirements, pH-values, etc., but must include all other important factors, especially those influencing the mechanical properties of the films. It appears absolutely necessary therefore to create standard specifications regulating the methods of evaluation equally valuable to the producers and consumers of these paint materials and of the raw materials going into their production.

7) Special attention must also be paid to the water contents of pigments and vehicles as well as to the contents of electrolyte. There is still need for research and investigations into the influence of the water of constitution and absorption as well as of the water produced by reactions within the films on the properties of the coatings.

8) Closely connected with this factor is the testing of the packing and arrangement of the pigment particles. It is absolutely necessary to determine the importance of dense packing of the pigments, possible faults within the structure and the various shapes of the pigment grains on the character of the paint films.

TECHNOLOGY

TITANIUM PIGMENTS. Titanium pigments are discussed under such topics as titanium minerals, manufacture of titanium oxide, properties of titanium oxide pigments and formulation of paints containing titanium pigments. R. Mansell. Paint, Oil and Chem. Rev. **110**, 18, 40-41 (Feb. 6, 1947).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PRINCIPLES OF FLUID MIXING AND THE APPLICATION OF MIXING DEVICES*

By H. E. SERNER, Davidson and Serner Company

Every industry is concerned with the improvement of its products, and the reduction of production costs.

I am going to discuss the process of fluid mixing as it is applied in the industries you represent, and also the possibilities of using improved methods and improved equipment.

Many of the very difficult processes such as heat transfer, fractionation, absorption, and others have been thoroughly explored and means for rational design approach have been made available. It is characteristic of most scientific investigations that more attention is paid to problems for which a need of solution is evident, than to those where the solution does not appear to be quite so necessary. Mixing, one of the oldest processes known to man has, until recently, remained merely an art to be employed as best one can.

However, many of the countless devices, and mechanical arrangements that are used for this purpose have been mechanically perfected to a high degree. But due to the fact that the basic principles of mixing have not yet been fully determined, little progress has been made regarding the development of new methods and means. Complete understanding of a process and the correct analysis of all factors involved are essential to its rational solution.

But because the art of mixing has not yet reached the stature of an exact science and therefore is not fully understood, it is necessary to begin with a rather general discussion before any conclusions can be reached, or suggestions can be made that might be of profit to the industry.

Mixing has never been a problem—until the advent of mechanized industry. Whenever a mixing job had to be done in the old days, a suitable vessel and a stick in the operator's hand were all that was required; sooner or later the mixing job would be accomplished.

To mix some things, especially miscible fluids, appeared so simple, so obvious to the casual observer, that for a long time it was not considered a problem.

When industry began to progress, and when at last mechanical power became available, the same old stick, that had been used for centuries, was then called a paddle, and it was driven at almost the same slow speed from an overhead line-shaft. As the production of a plant increased, more mixing tanks were added to the line. This type of arrangement is still in existence in many large plants.

However, a revolutionary change took place when electric power and electric motors of many sizes and speeds became available. The advantages of the individual drive were only too evident; but —as is the case with all gradual developments, we like to adhere to the good old methods we know and trust, and we are afraid to make sudden and radical changes. The result is usually a compromise between the old and the new, and the improvement is slow.

The application of individual motor drives for mixing units created new problems: A line-shaft drive is very well suited to the operation of paddles and similar slow-speed devices, whereas the electric motor is essentially a high-speed device. When, for example, a large paddle-mixer is to be individually driven at a speed of from 30 to 40 r.p.m., the designer faces the problem of reducing the high motor speed, and in many cases the mechanical complications of such a drive, together with its cost, provide a good argument against it.

* This paper was presented before the Twenty-sixth Annual Meeting of the Federation of Paint and Varnish Production Clubs, Chicago, Ill., for publication in the *Official Digest* of the Federation of Paint and Varnish Production Clubs and is published by their permission.

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This led first to the use of the turbine impeller which can be operated at higher speeds than the paddle, and does, in this case, not require excessive power; and it finally led to the use of the propeller which can be operated at still higher speeds. But, unfortunately, all of these devices are limited in their scope of application.

Furthermore, the power required by any mixing unit is not too important as long as the drive is from a line-shaft with plenty of excess power available; whereas in the case of the individual drive the correct power requirements have to be determined. But the only way in which this could be done was by actual trial, or on the basis of past experience.

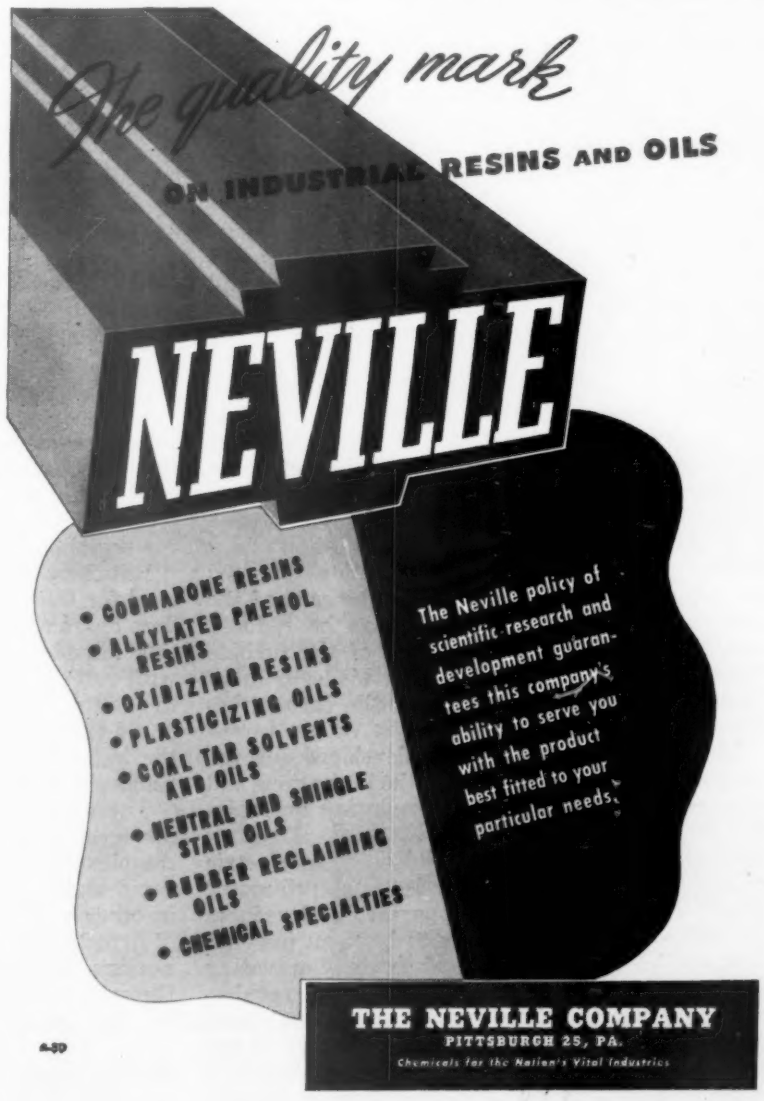
It became apparent that mixing, and even the simple agitation of fluids, which in the past had appeared to be so very simple, actually presented problems in applied physics that are not yet full understood.

In order to better explain the process of mixing, I shall quote the definition given by Valentine and McLean, "In all cases two or more materials existing either separately or in an unevenly mixed condition, are, by mixing, to be put into such a condition that each particle of any one material lies as nearly adjacent as possible to a particle of each of the other materials."

This defines the result of the process, but it does not, of course, explain how it can actually be accomplished. The difficulty lies in the fact that mixing, in its usual forms, is a three-dimensional process, and in order to understand it better it must first be considered on a two-dimensional basis. A good example is the circular stone-mill. When two or more materials are fed between two flat surfaces, one of which is in rotation, the particles in contact with the rotating surface travel faster than those in contact only with the stationary surface, and a shear-plane is created between these two horizontal material layers. But since all particles also move toward the periphery of the stone-mill in a helical path, innumerable shear-planes are also created in vertical planes, and as a result the discharged product can be mixed in the proportion in which materials are fed to the mill—the stone-mill may be considered a good mixing device under certain operating conditions—*materials are being mixed as they pass through the mill.*

A similar condition to that which exists between the two surfaces of a stone-mill also exists between all the various streams and currents that are produced by an agitator throughout the entire liquid contents of a mixing vessel. The speed with which the mixing job can be accomplished depends on the number of such shear-planes created within the body of the liquid, and the relative velocity of the movement of the liquid layers.

The stone-mill, however, is not a fluid agitator and cannot be used to agitate and mix the contents of a large vessel; whereas the conventional agitators that are used for fluid mixing can produce good agitation but they effect little mixing *"per se."* The mixing they do effect is the result of the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differential flow created by them in the liquid, and the resultant shear-planes.

It is now possible to enumerate the most important features of a good mixing apparatus:

1. The entire content of the mixing vessel must be properly-agitated.
2. The most complex flow-pattern must be created.
3. The impeller itself must be able to effect as much mixing as possible.

It is not difficult to accomplish most of this when the materials have low viscosities and are miscible. When some of the components of the mixtures are solids, and when high viscosities are encountered, then the problem becomes more difficult.

It is well known to every operator that the paddle agitator can be relied on to produce uniform agitation in very thick fluids throughout the entire mixing vessel, because the paddles usually extend through the vessel within a few inches of its shell. Turbines and propellers often fail to produce proper circulation in viscous liquids, since these devices are usually of small proportion with respect to the size of the vessel. Their "effective radius of agitation" is often limited. This effective radius depends on the velocity with which the fluid is expelled from the impeller, and it also depends on its mass.

To produce the necessary, high liquid discharge velocities with either turbines or propellers, requires often excessive power, which makes the application of these devices uneconomic for high viscosities; then the slow-speed paddle agitator must be resorted to.

When the agitation produced by an impeller does not extend throughout the entire vessel, it is a sign that its effective radius of agitation is not sufficient. In order to increase this effective radius of agitation, the impeller must be driven at a higher speed to increase its discharge velocity. This increases the power consumption very rapidly, because the quantity of gallons pumped per minute is also increased. In the case of the turbine, this pumping capacity can be reduced somewhat by reducing the width of the turbine blades, but when the width of the blades is drastically reduced, the operation of the turbine becomes inefficient.

The disk-agitator has been developed for the purpose of overcoming some of the limitations and shortcomings of conventional agitating and mixing devices.

When an impeller is to be driven by an electric motor, it is desirable to drive it at the full motor speed; this simplifies the apparatus and reduces its cost. It is also desirable to have an impeller that can be adjusted to suit almost any operating conditions. The disk-agitator fulfils these requirements, and in addition it performs the one essential function which conventional agitators do not perform: it effects mixing in a manner similar to the circular stone-mill, but to a much greater degree. It therefore reduces mixing time in many difficult applications. With this disk-agitator it is also possible to produce any desired discharge velocity without undue increase in power consumption, because the quantity of the discharge can be controlled.

The disk-agitator however, is ideally suited for this type of work. It can operate with very high discharge velocities and at the same time with a limited discharge capacity, so that its effective radius of agitation can be very much increased without causing excessive power consumption.

Now, to consider the creation of a complex flow-pattern: if we were to pass a wooden stick rapidly through water, we would see in its wake countless waves and eddy-currents, which indicate the existence of many shear-planes. If we were to move the same stick through a thick oil paint, it would require much more power, and yet, the flow pattern in the wake of the stick would be a very simple one; an indication that not much mixing is taking place.

This is the reason why, even with a great power input, the mixing time often becomes unduly prolonged.

The disk-impeller consists solely of two or more parallel disks, mounted on a central shaft similar to a turbine. The disks are more or less closely spaced. This impeller imparts motion to the surrounding fluid only by the surface friction that exists between the disk surfaces and the liquid films with which they are in contact. The action of this device is somewhat surprising. In the case of low viscosity, water for instance, the discharge velocity from the disk-impeller can be higher than half the peripheral speed of the disks, but it can be reduced to almost the lowest desirable velocity by merely increasing the spaces between the disks. On the other hand, when the viscosity of the fluid is somewhat higher, it is possible to create a discharge velocity substantially equal to the peripheral speed of the disks.

But the greatest advantage of this device when used for the purpose of mixing, is in the peculiar flow characteristics of the fluid passing through this impeller. The fluid films in direct contact with two opposed disk-surfaces travel faster than the central portions of the liquid layer. As the liquid travels from the center to the periphery of the impeller in a helical path, its motion is continuously accelerated.

Therefore, the radial velocity differs with the distance from the center. The result is a very complex type of differential flow which effects a rapid and intense shuffling of the fluid particles, in other words mixing.

In most industrial applications the disk-impeller consists of several disks. The fluid passing through this impeller is therefore cut into a number of separate layers which diffuse into each other after being discharged. This high velocity discharge-stream creates a jet action on the surrounding fluid which greatly increases circulation

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and turn-over of the contents of the mixing vessel.

I want to point out here, that it is the inability of the compound action paddle-mixers to separate or cut viscous fluids into thin layers, which so unnecessarily prolongs the mixing time.

It is well known that the production of paints and varnishes has reached a point of economy where further small reductions in the cost of production cannot affect the profit very much. However, at the present rate of industrial development, with rapidly increasing labor rates and material costs—that which was true yesterday, will not be true tomorrow.

Let us consider the effect of this reasoning on an actual project: *The production capacity of an existing plant must be increased.* There are three possibilities:

1. Increase the output capacity of existing equipment.

2. Replace the old equipment with new equipment that has higher output capacity.

3. Build a new addition to the existing plant.

This last solution is the most costly one.

In order to improve existing equipment, we should first understand its shortcomings. First of all, the size of mixing vessels has, in the past, been seldom determined on a strictly rational and economic basis. The choice of size frequently appears to have been an arbitrary one, based on some apparent convenience, and neglecting other, more important but less obvious, factors. However, there exists for every mixing job a mixing apparatus of optimum size and shape. If we choose a mixing tank of average size for a very viscous material, we find that in order to do a good mixing job we have to use a slow-speed paddle-type or similar agitator, and then allow plenty of time for the mixing; it may vary from a half hour to twenty-four hours, as the case may be. We could, of course, reduce the mixing time by using a turbine, but in order to effect proper agitation of the entire large batch, the turbine would have to be operated at such a high speed that the power consumption would be prohibitive; since it increases as the cube of the liquid discharge velocity from the turbine. But this required discharge velocity drops rapidly as the diameter of the tank is reduced. For example: Under certain conditions the required discharge velocity from the turbine in a 4-ft. diameter tank would be 40 ft. per second; if the tank diameter were only 3 ft., the required discharge velocity would be only 35 ft. per second; and since the quantity of liquid in the smaller tank would be about half, the required power would be one-third.

Let us consider a fairly large tank with a slow-speed paddle agitator, mixing a very viscous liquid. If a high-speed agitator were to be used, it would require from two to three times as much power, but the mixing time would be cut in half.

Now, if a tank of half this capacity were to be used with a high-speed agitator, it would require

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less power than the large paddle-mixer, and the mixing time would be reduced to one-quarter. On an hourly basis, the output capacity of the small, highspeed mixer would be double that of the large paddle-mixer, and the power consumption, per gallon mixed, would be about one-third that of the paddle-mixer. The paint producer may, however, dislike to reduce the size of his tinting tanks, since it is much less troublesome to tint one large batch than two small ones. But this objection can be easily overcome. The holding capacity of the mixing tank does not have to be reduced. It is only necessary to change the shape of the tank and to place the impellers properly, in order to reduce the required effective radius of agitation. *It becomes quite apparent now that it is possible to increase plant production without having to provide more space, or new building additions, and without a great increase in labor cost.*

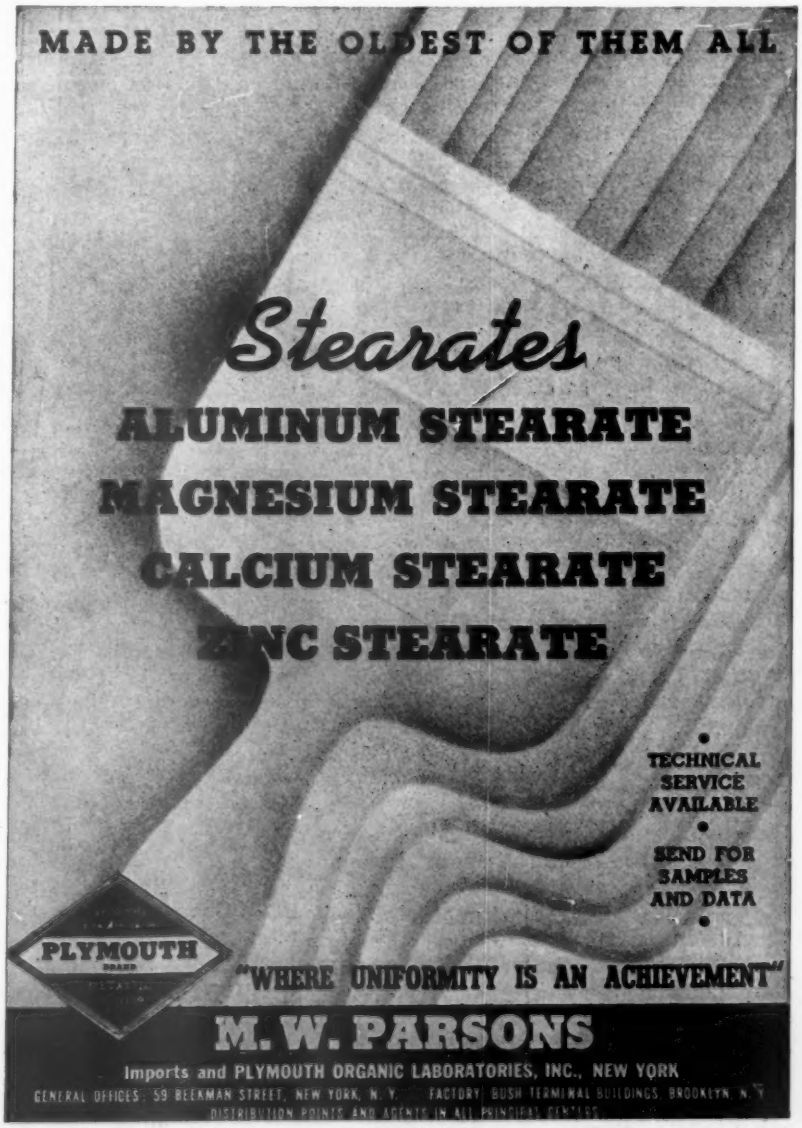
At this point I want to talk about a specific problem that concerns the paint industries:

The preparation of pigment pastes.

There are, to my knowledge, two basic methods in use. One method is based on the use of the ball-mill, in which not only the paste, but also the finished paint can be produced in one batch-operation. Unfortunately, this excellent method is limited in its application due to the difficulty it presents to color tinting. It is mostly employed for the production of large batches of paint that do not require tinting.

Another method consists of the use of high-powered paddle-type mixers with compound movement, followed by use of the roller-mill. The proportions of pigment and vehicle, and the sequence in which they are charged into the mixer, vary greatly.

Methods of operation are largely dictated by the physical limitations of this mechanical equipment. This process requires considerable time. The preparation of a single 100-gallon batch in the paddle-mixer requires from one to three hours, after which the entire batch still has to pass through a roller-mill. We know that the mixing time depends on the number of shear-planes created in the fluid mass. If we can double the number of shear-planes and increase velocities, we should reduce the mixing time to less than half. In modern, compound-type mixers, the possible limit has probably been approached for this type of apparatus. In order to improve this process we must look for a type of agitator that is capable of creating more shear-planes. Here again the disk-agitator has great possibilities, because in such highly viscous materials it performs, to a certain extent, the function of an attrition-mill, thereby assuring the thorough wetting of pigment particles and reducing particle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size to a minimum. Refinement in design may permit preparation of pigment pastes without the use of roller-mills. Size and capacity of such equipment would probably be very different, and the operating procedure would have to be changed to suit the new conditions; but the reduction in the cost of installation, the saving in space, plus the substantial reduction in operating time would be important factors in lowering production costs.

We come now to one of the biggest problems in the production of paint: continuous mixing.

This has probably been the dream of many production men, who may think of it as being far removed from practical application. But before arriving at such a quick conclusion, let us first consider its possibilities: Power consumption would be substantially reduced, but the reduction in cost of the mixing apparatus would be offset by the complicated feed-mechanism. Space requirements and, most important, labor costs would be very substantially reduced. The present development of proportioning pumps and constant-feed devices makes such an installation entirely feasible.

Continuous mixing has been successfully accomplished in other industries. There appear to exist two big problems in connection with continuous paint production: The first one is the difficult operation of pigment-paste preparation. I have previously pointed out that the high-speed disk-agitator should accomplish this paste mixing very much faster, and could do it best in a small vessel. It fulfils therefore the requirements necessary for continuous production.

The second problem is that of tinting the paint which, it appears, would have to be accomplished while the continuous flow of paint from the apparatus goes on; but this would be an erroneous conclusion. The rate of flow from such an apparatus can be varied at will. It is even possible to stop this flow completely and let it resume some time later without detriment to the product.

The application of some ingenuity in the use of these facts should make it possible to accomplish the tinting before the full flow of product is started.

The continuous production of paint appears to be entirely feasible, but the ultimate solution of the problem will not be an easy one.

It is not likely that either the chemist, the production engineer, or the equipment designer will solve it. The solution will become a reality when the plant management is convinced of the great advantages, inherent in this type of operation, and gives its full cooperation for the solution of this problem to the chemist, the production engineer, and the designer.

PREPARATION OF METAL SURFACES PREPARATORY TO FINISHING

By V. M. DARSEY, President, Rust-Proof Co.

It is generally recognized that the protection afforded most metals by painting is equally as dependent upon the preparation of the surface as on the composition of the paint. The importance of providing a thoroughly clean metal surface to obtain the maximum durability from paint coatings is fortunately becoming more widely recognized.

Many factors affect the durability of paint on metal surfaces; the one that has the most effect is the condition of the metal surface prior to the application of the paint. Surface treatment has been stressed by many investigators in preparing metals for painting. The preferred treatments provide for the removal of all rust, grease, scale and other foreign matter and chemical treatments to retard corrosion and promote greater adhesion of applied paint finishes. Permanent adhesion of paint finishes is a primary requisite for improving practice in painting most metals. To best accomplish this purpose, the method of metal preparation should by surface conversion treatment, reduce the corrosivity of the metal whereby underfilm corrosion at the paint-metal interface is retarded.

Paper presented at Industrial Finishes Section of N.P.V.&L.A. Ass'n Convention at Congress Hotel, Chicago, Tuesday, Nov. 9.

This is very important and will be developed to a greater extent with the slides. In other words, you are attempting always to stabilize the surface rather than to activate it if we are after a stable paint film. We know this is true, because on more stable surfaces, the paint film lasts longer, so it is superfluous to state that activating a surface is an ideal way for preparing it for painting.

In many instances, chemical treatment of metal surfaces is required to prevent paint discoloration and reaction of the paint vehicle with the metal to form a metal-resin complex at the interface.

Methods of Metal Preparation

A variety of industrial methods are utilized for cleaning and preparing metals for painting. Strictly speaking, the term "cleaning," as applied to the preparation of metals for painting, should be limited to the removal of dirt, oil and grease without chemical or mechanical change in the surface characteristics. Any method of preparation which changes the surface characteristics of the metal is likely to have a positive effect on the adhesion and resultant durability of applied organic coatings. For this reason it is advisable to distinguish between cleaning and other methods of metal preparation which either chemically or

mechanically change the characteristics of the surface. The most widely used methods of preparing metals for painting may be classified as:

1. Methods which do not materially change the surface characteristics of the metal.
2. Methods which mechanically or chemically alter the surface characteristics of the metal.
3. Methods which convert metal surfaces to a nonmetallic coating adapted to inhibiting corrosion and increasing the adhesion of applied organic finishes.

Group I includes various types of alkali, emulsion and organic solvent (trichlorethylene) cleaning which constitutes the simplest methods used in preparing metal for painting. These methods provide only for the removal of foreign matter, grease and oil, without importing any material change in the surface of the metal. The greatest possible success obtainable from the use of such methods is an absolutely clean metallic surface which does not provide for inhibiting corrosion or increasing the adhesion of applied paint finishes.

Group II includes mechanical methods of preparation such as sand and shotblasting which roughen metal surfaces so that paint will more readily adhere. Included in this same group are chemical methods of metal preparation, such as ordinary acid pickle and others involving the use of phosphoric acid and a grease solvent to clean and etch the metal surface to provide better adhesion of applied paint finishes. These methods impart a roughness to the metal surface which increases initial adhesion of applied paint finishes, but does not provide for inhibiting corrosion in the metal. Because of the increased activity of metal prepared by these surface roughening methods, it tends to corrode rapidly and metal so prepared must be painted immediately.

Group III includes those methods which convert metallic surfaces to a nonmetallic coating which inhibits corrosion and increases the adhesion and resultant durability of applied organic coatings. Such methods of metal preparation provide for the removal of all grease and foreign matter from the metal by Methods I or II prior to conversion of the surface to a protective coating. Instead of activating the metal such as results from acid etching and mechanical blasting, it converts the surface to a more stable and less reactive surface as a base for paint. Because of the increased resistance to corrosion, metal so prepared does not have to be painted immediately.

Factors in Preparation

The method or combination of methods used in preparing metal for painting should be selected depending upon the composition of the metal and the nature of the contaminants to be removed. Certain non-ferrous metals and alloys are chemically attacked by alkali or acid and such metals should not be subjected to any cleaning procedure that would affect detrimentally their composition or physical properties.

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Generally speaking, contaminants on metal surfaces may be termed visible and invisible. Visible contaminants such as grease, oil, and dirt cause much less trouble than invisible contaminants like alkali, acid, salts, and hand marks for they usually cannot be detected by appearance, and when present underneath an organic coating accelerate corrosion and promote blistering of the paint finish.

Many cleaning procedures will provide metal with a clean looking surface, and yet it will not be satisfactory for painting. Any cleaning procedure in which the final water rinse contains small amounts of alkali or soluble salts will leave invisible and active residue on the surface of articles rinsed therein which is apt to cause premature failure of the paint. It is a fairly easy matter to protect against the presence of alkali in the rinse water by maintaining the solution at a pH below 5 with a mixture of chromic and phosphoric acids.

It is known that the degree of blistering in a paint finish adversely affects the protective life of the coating wherever moisture is a factor. The importance of proper rinsing of articles prior to painting cannot be over-emphasized wherever maximum performance of the finish is required.

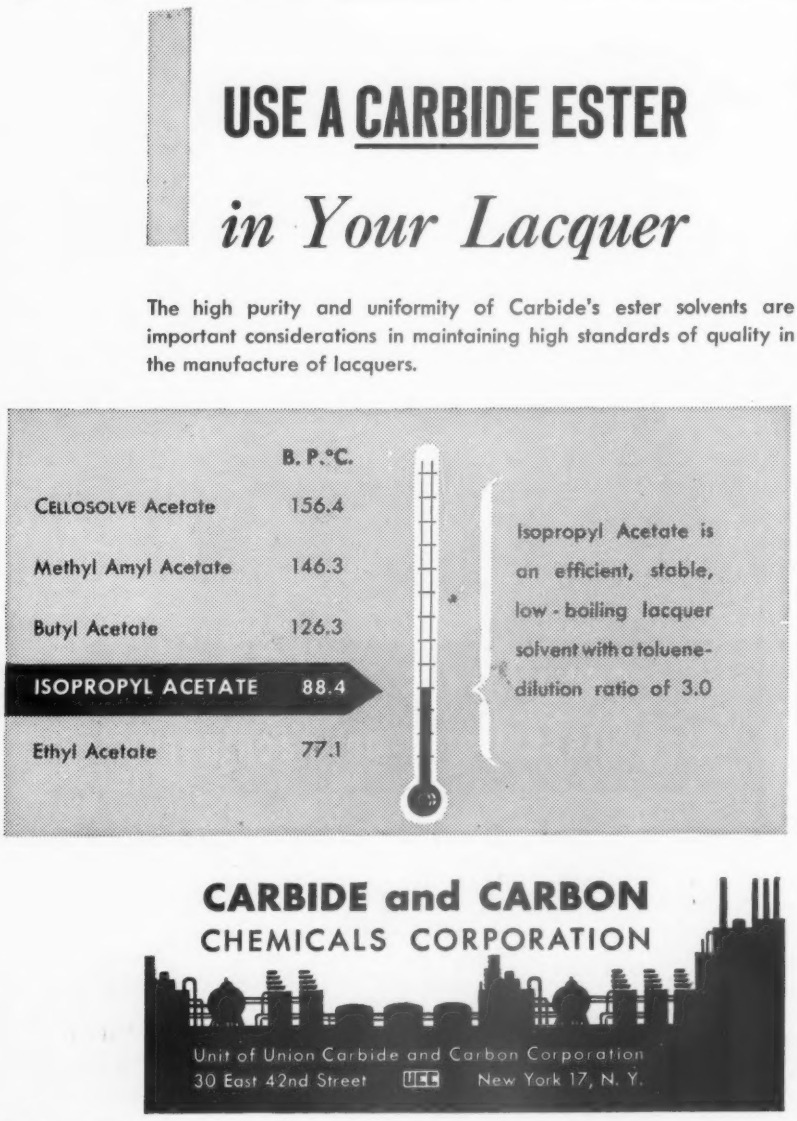
When Is a Surface Clean?

A test frequently specified to determine when a metal surface is clean is to immerse it in water and upon removal it shall support a film of water break-free. The test does not purport to reveal the presence or absence of acids, alkali or salts on such surfaces and for this reason it canont be relied upon as a test for determining the suitability of a surface prior to painting wherever maximum finish performance is desired. It has also been demonstrated that metal surfaces containing oil in combination with a wetting agent will support a film of water break-free.

When it is desired to test a given procedure for metal preparation for cleanliness and suitability for painting, perhaps no method serves the purpose better than immersing the painted article in water for 24 to 48 hours which is usually sufficient to reveal blistering in the paint coating at areas which contain active residue. This test, however, will not indicate the presence of traces of oil or grease remaining on surfaces from the cleaning operation. The effect of oil underneath the paint coating can usually be detected by an adhesion test such as the familiar knife test frequently used for this purpose.

Differences in Cleaning Metal

A word of explanation is believed advisable regarding the difference in surface characteristics of metal cleaned with phosphoric acid (with or without grease solvent) and metal freed of rust and soil by conventional cleaning methods, and then subjected to a balanced dilute acid phosphate solution (0.6 to 1.0 per cent acidity)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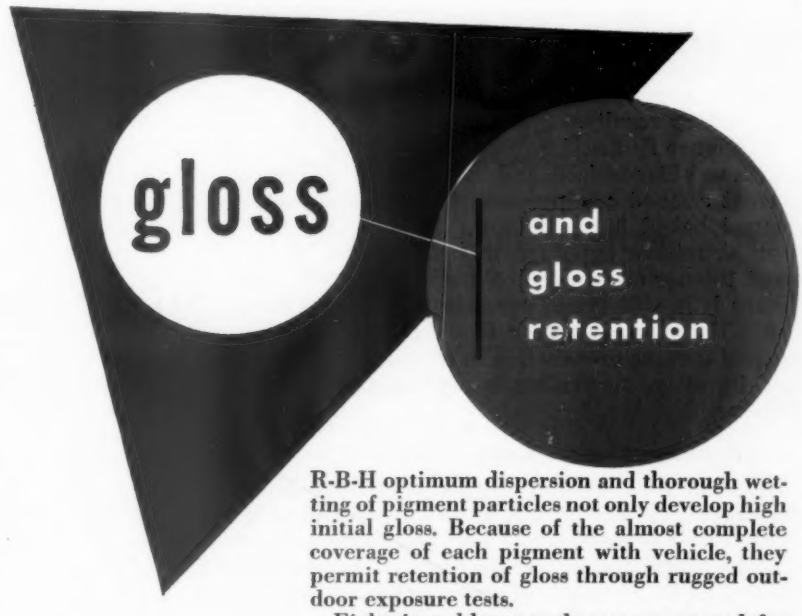
whereby the surface is converted to an insoluble crystalline phosphate coating. In the preparation of metal for painting by the use of phosphoric acid cleaners, the objective is the removal of rust and soil and the etching of the metal to which paint will more readily adhere. To accomplish this result, the concentration of the phosphoric acid employed (15 to 20 per cent) is such that it prevents the formation of any substantial phosphate coating on the metal. Tests made on steel after cleaning with phosporic acid have shown the phosphate film remaining from the cleaning operation to average only 5 to 10 mg. per square foot of surface. There results from the preparation of steel for painting by treatments with a phosphate coating solution (Bonderizing) from 100 to 400 mg. of coating depending upon the method of solution application. The primary requirements of metal preparation with phosphoric acid cleaners are the removal of rust and grease and etching of the surface; whereas, phosphate coating is the conversion of surfaces which have been freed of grease and soil by suitable cleaning methods to a corrosion inhibiting phosphate coating.

Phosphate Coating of Steel

Phosphate coatings for use as a base for paint are usually applied after fabrication of articles and immediately before painting, either by immersion of the object in the phosphating solution or by spraying the solution onto the article to be coated. In general, small parts which can be more conveniently handled as a unit load are treated by immersion application while larger parts such as refrigerator cabinets, automobile bodies and fenders are treated by spray application. The immersion process requires two to five minutes for the application of the coating and the spray process 45 to 60 seconds. In Figure 1 is shown two automobile fenders, one solvent cleaned only, the other Bonderized, and each finished with two coats of high bake black enamel. After six years Detroit roof exposure, the paint finish is intact over the Bonderized fender while considerable corrosion has taken place from the scratch made through the paint coating prior to the exposure on the solvent cleaned fender. In Figure II are shown two steel panels, on solvent cleaned, and the other Bonderized, each finished with two coats of lacquer and exposed outdoors at Morenci, Michigan, for 25 months. Corrosion has developed extensively at the scratch through the paint film on the solvent cleaned panel as well as from the edges of the panel, whereas little corrosion and failure of the paint has occurred on the phosphate coated panel. The protection afforded steel by a given paint finish is shown to be dependent upon the metal preparation prior to its application.

Preparation of Zinc and Alloys

Zinc and its alloys when painted are recognized to present a difficult adhesion problem due primarily to their reactivity with the vehicle of most



R-B-H optimum dispersion and thorough wetting of pigment particles not only develop high initial gloss. Because of the almost complete coverage of each pigment with vehicle, they permit retention of gloss through rugged outdoor exposure tests.

Eight iron blue panels were prepared for Florida exposure. Three were based on steel ball mill grinds of 24, 48 and 72 hours. Three were based on pebble mill grinds of same duration. Two were based on R-B-H dispersions.

As sprayed, the R-B-H panels showed highest Glossmeter readings of approximately 86, while the others ranged from 45.0 to 72.0. After polishing, all panels gave a reading of 83.5. After three months' Florida weathering, the R-B-H panels provided readings of 81.5 while the others varied from 57.0 to 67.5.

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organic coatings. Various methods of preparation are used to overcome this condition such as acid etching and weathering prior to painting. Such treatments roughen the surface and improve initial paint adhesion, but do not prevent reaction between the paint vehicle and the zinc. Many manufacturers convert zinc surfaces to a water soluble crystalline phosphate coating which inhibits corrosion and prevents reaction of the paint vehicle with the metal. Application of paint finishes over untreated and phosphate coated zinc show the advantage of surface conversion of the zinc prior to painting. In Figure III is shown the difference in paint performance when applied over untreated and phosphate coated zinc die castings after eight years outdoor exposure. The untreated die casting is characterized by loss in adhesion of the paint over considerable of the surface whereas the paint coating is still intact over the entire surface of the Bonderized casting. Not only does the phosphate coating of zinc surfaces improve the durability of applied paint coatings, but the treatment permits the use of a wider variety of paint coatings over phosphate coated surfaces with satisfactory results.

In Figure IV are shown two die castings, one of which was Bonderized, and the other an untreated solvent cleaned casting, each finished with alkyd enamel baked 30 x 250° F. After only seven months outdoor exposure, this paint finish has almost 100 per cent peeled off the untreated casting where it is still intact over the Bonderized casting. These tests further emphasize the importance of surface preparation in the painting of zinc and its alloys for promoting durability of paint finishes.

Preparation of Aluminum and Alloys

Most of the aluminum used in industry consists of alloys varying in composition and corrosion resistance. The adhesion of paint to alloys such as 17S or 24S is quite different from its adhesion to 3S and 52S, and unless properly prepared unsatisfactory paint performance is likely to result. Various methods are used in the preparation of aluminum for painting such as acid etching with phosphoric acid, chromate treatment or anodizing, to improve paint adhesion. A recent development consists in the conversion of aluminum alloy surfaces to an insoluble crystalline phosphate coating which effectively increases adhesion of applied paint finishes. Outdoor weathering tests indicate conversion of aluminum surfaces to a phosphate coating not only improves paint performance but permits the use of a wide variety of paints which cannot be used effectively over untreated aluminum.

In the past, most aluminum alloys have been finished with high zinc chromate content paints in order to provide the necessary protection against corrosion. In Figure V is shown two S25½ H aluminum panels, one solvent cleaned and the other Bonderized, each finished with 1.5 ml. of baked alkyd enamel and exposed for thirty months at Morenci, Michigan. Figure VI shows the difference in adhesion of paint over untreated and Bonderized aluminum. Not only does the phosphate coating of aluminum and its alloys permit the use of a greater variety of paint finishes, but it improves the adhesion and resultant durability of most paint finish.

Summary

In any successful finishing system, the preparation of the metal prior to painting is equally as important as the composition of the paint used. Removal of all foreign matter, grease and oil, is essential prior to the application of organic coatings to afford normal protection. Conversion of ferrous surfaces to a corrosion inhibiting phosphate coating increases the adhesion and resultant durability of organic coatings. Conversion of nonferrous metals to a phosphate coating inhibits reaction of the paint vehicle with the metal and increases the retained adhesion and durability of applied organic finishes. Various methods of preparing metal for painting are available, and the requirement of the organic coating in the environment in which is is used should govern the method used.

Following his address, Mr. Darsey showed slides.

NEWS AND REVIEWS

Atlas Powder Company is offering a new 28-page booklet on the use of sorbital as a polyol in synthesis of solid and liquid vehicles for protective finishes. Specific and practical directions are given for preparation of hard gums, "in situ" varnishes, tall oil esters and alkyd resins from sorbitol and sorbitol combinations with other polyols. In addition, objective valuations are given for many formulations based on sorbitol, and comparisons of sorbitol with other polyols used in this field.

Advantages claimed for products made from sorbitol-synthesized vehicles are outstanding compatability, rapid drying, high adhesion strength, flexibility and durability. These vehicles characteristically wet pigments easily, with consequent ease of grind and enhanced gloss.

* * * * *

A new type of synthetic resin for fast-drying enamels was announced today by the Coating Resins Department of American Cyanamid Company. The new resin is the result of extensive research on chemical copolymers of styrene and alkyds, and will be marketed under the trade mark of Cycopol.

This resin is especially adapted for use in industrial finishes, and in fast-drying household enamels. The outstanding qualities of the Cycopol resin in addition to its very fast drying are pale color, excellent toughness and adhesion.

RECENT ADVANCES IN PAINT TECHNOLOGY

PETROLEUM AROMATIC EXTRACTS. A brief article on the use of petroleum aromatic extracts for partial replacement of linseed oil and rosin. Compatibility with linseed oil, effect on paint formulation and use of extracts in core oils and compounds are discussed. Anon. Paint Manuf. **17**, 241-242 (1947).

TREATMENTS OF METAL SURFACES PRIOR TO PAINTING. The application of a chemical treatment that deposits a uniform, finely crystalline, insoluble, non-metallic coating of the proper texture, is recognized as a distinct step in the progress of protecting surfaces against corrosion with organic materials. However, chemical treatments do not in themselves retard corrosion, but the chemically created coatings give the adhesive base needed by the anti-corrosive paints. Chemical pretreatments for steel, galvanized metal and sheet zinc, aluminum and aluminum alloys, lead, copper, brass and magnesium alloys are discussed. E. F. Hickson and W. C. Porter. Product Engineering **18**, No. 8, 128-130 (Aug., 1947).

REMOVAL OF FUME FROM LINSEED OIL KETTLES. A report of an investigation of the elimination of fumes from the heat- or air-bodying of linseed oil. After trying various methods, a satisfactory solution was found in the adaptation of a commercial fume scrubber. J. C. Dittmer. Chem. Eng. **54**, No. 3, 110-113 (1947).

SOME UNSAPONIFIABLE CONSTITUENTS OF THE DEODORIZATION DISTILLATES OF VEGETABLE OILS. An examination was made of the unsaponifiable constituents of the deodorization distillates of coconut oil, palm kernel oil, palm oil, groundnut oil, cottonseed oil and sunflower seed oil. The presence of large amounts of methyl ketones (chiefly methyl nonyl ketone) and carbinols corresponding to these ketones has been confirmed in the case of the first two oils, and lesser amounts in the others. The first two oils give distillates which contain lauric acid as the major component fatty acid, and with the others the bulk of the unsaponifiable matter consisted of hydrocarbons. The predominant type of hydrocarbons was shown to be terpenoid. Detailed data are tabulated on these and other constituents found or approximately identified in the distillates. H. Jasperson and R. Jones. J. Soc. Chem. Ind. **66**, 13-17 (1947).

THE MIXED UNSATURATED GLYCERIDES OF LIQUID FATS. LOW-TEMPERATURE CRYSTALLIZATION OF RAPE OIL. The mixed glycerides of rape oil were separated by systematic crystallization from acetone at low temperatures into three fractions, each less com-

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plex in composition than the whole fat. The component acids of each fraction were determined, after preliminary resolution into two groups by low-temperature crystallization from acetone or ether, by ester-fractionation. Spectrographic analysis of alkali-isomerized acids from selected ester-fractions showed the presence of more linelenic acid than had hitherto been reported, and also of small amounts of a docosadienoic acid, $C_{22}H_{40}O_2$. The component acids of the rape oil included myristic, palmitic, stearic, arachidic, behenic, lignoceric, hexadecenoic, oleic, linoleic, linolenic, erucic and docosadienoic acids. The component glycerides were made up, approximately, of 54% (mol.) containing one unsaturated C_{18} and two unsaturated C_{22} acyl groups, 28% (mol.) containing two unsaturated C_{18} and one unsaturated C_{22} acyl group, and 18% (mol.) containing one group each of saturated and unsaturated C_{18}, and unsaturated C_{22} acids. T. P. Hilditch, P. A. Laurent and M. L. Meara. J. Soc. Chem. Ind. **66**, 19-22 (1947).

THE CORROSION OF IRON AND STEEL AND ITS PREVENTION. The results of a thorough investigation into factors affecting metal corrosion and the prevention of such corrosion chiefly by paint (the major protective measure against corrosion of metals) are given. Many phases of this investigation are discussed including consumption of paint for preventing corrosion, use of composite protective schemes, comparison of different materials when immersed in seawater or buried in soil, effect of climate on rate of rusting, atmospheric corrosion, main types of protective measures (environmental changes, cathodic protection, protective coatings), protective coatings other than paint (hot-dipping, cementation, electro-deposition and metal spraying), importance of coating thickness, effect of surface roughness on desirable thickness of paint films, and indoor and outdoor paint requirements. Tables, graphs and illustrations pertaining to the results are included, as well as a lengthy discussion. J. C. Hudson. J. Oil & Colour Chem Assoc., **30**, 35-52 (1947).

INFRARED DRYING OF LACQUERS. The drying rate and film hardness of a number of different colored lacquers after stoving in an oven and after infrared irradiation have been compared and the temperature attained in the two processes measured. Ten minutes under the infrared (250-w.) lamps produced about the same hardnesses as 60 minutes in the oven at 120°. Under the lamps the black lacquer heated up and hardened more rapidly than the other colored lacquers in the initial stages, but ultimately the white and blue lacquers were the hardest and the red lacquer was the softest both under infrared irradiation and in the oven. The temperature of the films under the infrared lamps measured by a thermocouple rose more rapidly and was greater than that of a therometer at the same distance, and varied with the color of the lacquer but the temperature of the film in the oven rose more slowly, was less than the oven air temperature and was independent of color. H. W. Talen. Verfkroniek **15**, 62-5 (1942) (abstr. through Chem. Abs. **42**, 4367-8 (1948)).

ELASTIC PROPERTIES OF PAINT FILMS FOR METALS. Detachable films of drying oil derivatives were prepared on the surface of mercury or an amalgamated metal, in order to observe their properties. Tensile strength tests were run. The extension of the film can be read off directly, and there is also a recording mechanism providing a load/elongation graph, which can be converted into a stress/strain diagram. In determining tensile strengths, the following factors needed to be controlled before reproducible results could be obtained: (a) all film dimensions, (b) temperature and humidity at the time of testing, and (c) rate of extension of the film. Film properties of stand oils of comparable viscosities are similar, varying little with the details of the particular heating process. As the viscosity increases, there is an increase in both the tensile strength and the ultimate extension to a maximum of about 14 kg. per sq. cm., and 85% extension. Variations of the proportions of drier metals (lead, manganese, cobalt) affect not only the rate of drying but also the nature of the dried film. Additions of pigment give hardness to a film and pigmented films are much stronger and much less extensible than the corresponding unpigmented ones. The elastic properties of a varnish film are very different from those of a film of the oil from which, by incorporation of resins, the varnish is made. The strength is greatly enhanced, progressively as the resin proportion is increased. The customary ways of testing the ability of a paint film to undergo deformation are to apply the bend test. Paint is applied to a small metal panel and dried. The panel is then bent over a mandrel of known diameter with the film on the outside and the surface is then examined at the bend for cracks. It should not be overlooked that bend tests may not give reliable information, unless the adhesion of the paint film to the panel is great enough to prevent the film from failing by lack of adhesion before its ultimate extension is reached. In paint films it is not always easy to see the connection between brittleness and measurable elastic properties. A highly pigmented film often has very low extensibility under all conditions and is usually described as brittle. It is thus shown that the elastic properties of a paint film can, in its formulation, be varied over a wide range, and this article has attempted to show the possibility of studying detached films, with a view to understanding of their elastic nature, in order that metallic and other surfaces can be more completely protected, under conditions of mechanical stress by paint films. S. Conolly. Metal Treatment **14**, 222-6 (1948) (abstr. through Chem. Abs. **42**, 4368 (1948)).

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